The symmetry properties of the effective diffusivity tensor in anisotropic porous media

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(Received 13 June 1986; accepted 4 December 1986)

The effect of anisotropic grain structures on the average transport properties resulting from flow through porous media is derived using methods that involve ensemble averaging the basic conservation equations and a multiple-scale analysis. The Lagrangian or "moments" effective diffusivity tensor, defined as the long-time limit of the time rate of change of the mean-squared displacement of a tracer particle, is equivalent to the symmetric part of the Eulerian diffusivity, defined as the mass flux induced by a linear concentration gradient in the limit of long times. In an anisotropic medium there may be a component of the mass flux perpendicular to the imposed concentration gradient, resulting in an effective diffusivity tensor that is not symmetric. Such an effect is not detected by the moments or Lagrangian approach.

I. INTRODUCTION

The transport of heat and mass through porous media is of importance in a number of applications including enhanced oil recovery, ground water flows, packed bed reactors, and contacting devices such as ion exchange and adsorption columns. In previous papers[1,2] we derived the macroscopic transport properties governing heat and mass transfer on a scale large compared to the grain size l in disordered porous media consisting of fixed spherical particles and cylindrical fibers, respectively.

In the present paper we consider more general microstructures that may be anisotropic. In addition, we develop alternative Eulerian and Lagrangian definitions of the effective diffusivity. In Sec. II we use the method of multiple scales to obtain expressions for the solute average velocity and diffusivity in the limit of long times. We derive a single expression for the effective diffusivity, which includes the coupled effects of both conduction (or diffusion) and convection, and show that the Lagrangian diffusivity is equal to the symmetric part of the Eulerian diffusivity tensor. The Eulerian diffusivity is the ensemble average of the autocorrelation of a velocity $\mathbf{v}_m$, which is the sum of the fluid velocity and a "drift" velocity resulting from spatial variations in the molecular diffusivity and solubility of the diffusing species.

In Sec. III we derive a set of relations that play the same role in flow-dispersion problems as the Onsager relations do in irreversible thermodynamcis. These relations admit the possibility of an antisymmetric component to the Eulerian diffusivity in anisotropic media that do not possess three orthogonal planes of reflectional symmetry—a requirement that a net torque is exerted on the medium by a uniform average flow. This antisymmetric diffusivity gives rise to a component of the mass flux perpendicular to the concentration gradient. This phenomenon has a formal analogy with the Hall effect in solid state physics, although it arises from an unrelated physical mechanism.

The calculation in Sec. IV of the effective diffusivity of a periodic array of screw propellers provides a convenient illustration of the antisymmetric contribution to the diffusivity that arises in anisotropic media without reflectional symmetry, although this effect is not limited to ordered media. In the limit of the high Peclet number $\mathrm{Pe} = Uh/D_f$, the antisymmetric diffusivity is purely mechanical, i.e., it is independent of the molecular diffusivity D_f. Here h stands for both lattice spacing and microstructural length scale. The mechanical *antisymmetric* diffusivity, however, is of a different nature than the familiar mechanical *symmetric* diffusivity. The antisymmetric diffusivity is odd in the bed average velocity U, being proportional to Uh, and arises from the anisotropy of the bed structure, while the mechanical part of the symmetric diffusivity is even in the velocity U, being proportional to $|U|h$, and arises from the disordered nature of the grain structure.

II. MACROSCOPIC TRANSPORT PROPERTIES

In this section we shall develop a method for determining the effective transport properties that govern heat and mass transfer on a length scale large compared to the grain size l of a porous medium. We shall speak in terms of the mass transfer problem, but the analogy[1,2] between heat and mass transfer makes the present analysis equally applicable to the heat transfer problem. The derivation of the macroscopic transport properties in this section is applicable not only to porous media but to any system in which a small scale structure affects the macroscopic transport observed on a much larger scale. Application of the present results to other systems requires knowledge of the solute's velocity $\mathbf{v}$ and the ensemble of realizations of the system.

We shall consider two alternative definitions of these macroscopic transport properties: (1) an Eulerian definition in terms of the relationship between the average mass flux and the average concentration field, and (2) a Lagrangian definition in terms of the moments of the probability distribution for a single tracer particle. The Eulerian definition has been used primarily in studies of transport in the absence of fluid convection, while the Lagrangian definition

 0031-9171/87/030642-09$01.90

has typically been used for studies of transport in the presence of convection. We shall see here that the Eulerian definition is not strictly equivalent to the Lagrangian, containing an antisymmetric component in the diffusion tensor.

A. Eulerian approach

The conservation equation for a solute species in a multiphase medium may be written in the form (cf. van Kamper[3], Eq. X.4.7)

$$\frac{\partial c}{\partial t} + \nabla\cdot\mathbf{q} = 0\,, \tag{1a}$$

$$\mathbf{q} = \mathbf{u}c - (D/M)\nabla(Mc)\,, \tag{1b}$$

where c is the concentration of the solute, $\mathbf{q}$ is the mass flux, D/M is a generalized function that takes on the values D_f in the fluid and $m^{-1}D_p$ in the solid, and M, the solute's activity coefficient, is a generalized function that takes on the value 1 in the fluid and m in the solid. Here, D_f and D_p are the molecular diffusivities of the solute in the fluid and solid phases, respectively, and m is the partition coefficient giving the ratio of the solute concentration in the fluid and solid at the interphase boundaries. In the present application $\mathbf{u}$ is simply the fluid velocity, but one could also include the effect of an external force on the solute, causing the solute's deterministic velocity to differ from the fluid's. The fluid velocity $\mathbf{u}$ may be determined by solving the Navier–Stokes equations for incompressible flow through the porous medium

$$\rho\frac{D\mathbf{u}}{Dt} = -\nabla p + \mu\nabla^2\mathbf{u}\,,$$

$$\nabla\cdot\mathbf{u} = 0, \quad \mathbf{u} = 0 \text{ on solid surfaces}\,,$$

with a specified average velocity $\langle\mathbf{u}\rangle = \mathbf{U}$. Here p is the dynamic pressure, containing the body-force density, ρ is the fluid density, and μ is its viscosity. In most cases of interest the Reynolds number for motion based on the grain size is small, and the above equations will reduce to Stokes equations.

Equation (1) applies throughout the medium—both fluid and solid phases—and gives continuity of mass flux and local equilibrium at the interphase boundaries. The requirement that the third term in Eq. (1b) be nonsingular gives local equilibrium and continuity of mass flux at the interphase boundaries. The step change in M at the boundaries necessitates a step change in c, in order that the Mc is continuous and $\nabla(Mc)$ is nonsingular; this step change in c is the interphase partitioning of the solute at local equilibrium. The step change in D/M in turn requires a step change in $\nabla(Mc)$, so that the flux $(D/M)\nabla(Mc)$ is continuous at the boundary and its divergence is nonsingular.

We seek the average mass conservation equation that applies to concentration fluctuations that occur on a "macrolength" scale L, which is much larger than the scale l of the medium microstructure. We shall derive this macrotransport equation by averaging over the detailed fluctuations in the velocity and concentration field occurring on the small length scale l.

To this end we define an ensemble average, denoted by $\langle\ \rangle$, as the average over all possible configurations of the interphase boundaries. The configurational average concentration may be written as

$$\langle c(\mathbf{x},t)\rangle = \int d\boldsymbol{\zeta}\, c(\mathbf{x},t\,|\boldsymbol{\zeta})g(\boldsymbol{\zeta})\,, \tag{2}$$

where $\boldsymbol{\zeta}$ is a vector that contains all the information necessary to specify the grain structure, i.e., the position, orientation, and shape of each grain. The weighting function $g(\boldsymbol{\zeta})$ is the probability that the bed has the configuration $\boldsymbol{\zeta}$.

An equation for the "configurational" ensemble average concentration $\langle\ \rangle$ is obtained by averaging (1) to yield

$$\frac{\partial\langle c\rangle}{\partial t} + \nabla\cdot\langle\mathbf{q}\rangle = 0\,, \tag{3a}$$

$$\langle\mathbf{q}\rangle = \langle\mathbf{u}c - (D/M)\nabla(Mc)\rangle\,. \tag{3b}$$

In order to complete the macroscopic description of the transport process we must relate the average mass flux to the average concentration, and so *define* the solute velocity and diffusivity. To do so, we take advantage of the widely disparate length scales l and L to obtain an approximation to (3) in the limit $\epsilon = l/L \ll 1$. The detailed concentration field c varies over the grain size l, while the average concentration $\langle c\rangle$ varies only over a much larger length L—the detailed fluctuations having been smoothed by averaging. Thus, it is natural to use the method of multiple scales (Keller[4]) and to introduce two position variables: the local or microscale position $\mathbf{x}$ nondimensionalized with l, and the macroscale position $\mathbf{X}$ nondimensionalized with L. Similarly, we define micro- and macroscale times t and T nondimensionalized with l/U and L/U, respectively. The microscale time is the characteristic time required for a solute molecule to sample the microstructure. This could be a diffusive time l^2/D_f as well as the convective time l/U we have chosen here. As long as the Peclet number Ul/D_f is small compared to ϵ^{-1}, however, both these times are short compared to the macroscale time, and the results of the analysis are independent of which of these times we use to nondimensionalize t.

With the multiple-scale variables, the basic conservation equation for $c(\mathbf{x},t,\mathbf{X},T)$ becomes

$$\frac{\partial c}{\partial t} + \nabla\cdot\mathbf{q} = -\epsilon\left(\frac{\partial c}{\partial T} + \nabla_{\mathbf{x}}\cdot\mathbf{q}\right), \tag{4a}$$

$$\mathbf{q} = \mathbf{u}c - (D/M)\nabla(Mc) - \epsilon(D/M)\nabla_{\mathbf{x}}(Mc)\,, \tag{4b}$$

where the term on the right-hand side of (4a) is the slowly varying macroscale part. Having assumed that $\langle c\rangle$ varies only on the macrolength scale L, temporal changes in the average concentration can only occur over the long times L/U or L^2/D_f required for solute to be transported over a length L between regions of varying average concentration. Thus, the averaged or smoothed quantities only depend on the macrocoordinates $\mathbf{X}$ and T, and upon averaging, (4a) takes the simple "macroconservation" form

$$\frac{\partial\langle c\rangle}{\partial T} + \nabla_{\mathbf{x}}\cdot\langle\mathbf{q}\rangle = 0\,. \tag{5}$$

Here, $\nabla_{\mathbf{x}}$ and ∇ are the Nable operators with respect to the macroscale position $\mathbf{X}$ and the microscale position $\mathbf{x}$, respectively.

If the average concentration is nonsingular throughout space, the linear relationship between the average flux and

average concentration may be written as

$$\langle \mathbf{q} \rangle = \mathbf{V}\langle c \rangle - \epsilon \nabla_{\mathbf{x}} \cdot (\mathsf{D}\langle c \rangle) + \epsilon^2 \nabla_{\mathbf{x}} \nabla_{\mathbf{x}} : (\mathsf{H}\langle c \rangle) + \cdots , \quad (6)$$

where the phenomenological coefficients $\mathbf{V}$, D, H, etc., have been nondimensionalized with respect to V, VL, VL^2, etc. Here, V is the magnitude of the as yet to be found solute average velocity. These coefficients are at most functions of the slow space and time scales $\mathbf{X}$, T. For the statistically homogeneous media considered here, these coefficients are constant, but macroscale variability can readily be included. If the coefficients D and H do vary on the macroscale it is most convenient to write them inside the differential operators as we have done in (6) in order to group like powers of ϵ (cf. van Kampen,[3] Chap. VIII). Equation (6) serves as the *definition* of the solute velocity $\mathbf{V}$, diffusivity D, and higher moments.

Although the second, diffusive term on the right-hand side of (6) is small compared to the first, convective term, it cannot be neglected because it changes in a fundamental way the *qualitative* nature of the solution for the concentration field. If we kept only the convective term in (6), we would find that the solute is translated, but it does not spread with time unless the diffusive term in retained. The third and higher order terms give the skewness in the dispersive spread and are only important at short times. The dominant long-macroscale-time limit, $t \to \infty$, $T \sim O(1)$, i.e., $\epsilon \to 0$, is given by the second term, and thus (6) can be truncated at second order.

The value of extending the multiple-scale analysis beyond the calculation of the $O(\epsilon)$ diffusive term in (6) is questionable, as the inclusion of a few additional terms in the expansion is unlikely to yield the correct qualitative behavior of the average concentration in cases where there is not a wide separation of length scales, $\epsilon \ll 1$. Also, the inclusion of additional terms in (6) would require the specification of additional boundary conditions if (5) and (6) were to be used to solve a macrotransport problem on a finite spatial domain. A more natural way to treat the "transient" dispersion that occurs in the absence of a wide separation of length scales is the use of nonlocal description of the macrotransport processes, replacing the infinite series in (6) with a convolution integral over space and time involving a spatial- and temporal-wavelength-dependent diffusivity (cf. Koch and Brady[5] and Koch[6]).

To evaluate the solute average velocity $\mathbf{V}$ and effective diffusivity D we solve (4) for the detailed concentration field subject to the requirement that it sum to the average, and then compare (3b) to (6). If we expand the detailed concentration field and mass flux in powers of ϵ,

$$c(\mathbf{x},t,\mathbf{X},T) = \sum_{n=0}^{\infty} c_n \epsilon^n , \quad \mathbf{q}(\mathbf{x},t,\mathbf{X},T) = \sum_{n=0}^{\infty} \mathbf{q}_n \epsilon^n ,$$

then the zeroth order problem in ϵ is

$$\frac{\partial c_0}{\partial t} + \nabla \cdot \mathbf{q}_0 = 0 , \quad (7a)$$

or, at long microscale times, simply

$$\nabla \cdot (\mathbf{q}_0) = 0 , \quad (7b)$$

$$\mathbf{q}_0 = \mathbf{u}c_0 - (D/M)\nabla(Mc_0) , \quad (7c)$$

with

$$\langle c_0 \rangle = \langle c \rangle . \quad (7d)$$

Note that $\langle c \rangle = \langle c(\mathbf{X},T) \rangle$ can depend only on the macroscale variables. The solution of (7) is one which is at local equilibrium on the microscale and whose average (7d) varies on the macroscale,

$$c_0 = P_{eq}\langle c \rangle , \quad (8a)$$

where P_{eq} satisfies

$$\nabla \cdot [\mathbf{u}P_{eq} - (D/M)\nabla(MP_{eq})] = 0 , \quad (8b)$$

with

$$\langle P_{eq} \rangle = 1 . \quad (8c)$$

Here, P_{eq} is just the equilibrium distribution of the solute in the absence of concentration variations on the macroscale. This equilibrium distribution is a constant in each phase for an incompressible fluid in the absence of an external field. In this case P_{eq} simply reflects the partitioning between the two phases

$$P_{eq} = \begin{cases} 1/(1-\phi+\phi m^{-1}), & \text{in the fluid} , \\ 1/m(1-\phi+\phi m^{-1}), & \text{in the solid} , \end{cases} \quad (9)$$

where ϕ is the volume fraction of the solid phase. The solution [Eq. (9)] for P_{eq} is such that MP_{eq}, the "activity" of the solute, is constant throughout the microstructure at local equilibrium.

The resulting zero-order contribution to the average mass flux is

$$\langle \mathbf{q}_0 \rangle = \langle \mathbf{u}c_0 \rangle - \langle (D/M)\nabla(Mc_0) \rangle , \quad (10a)$$

$$= \langle \mathbf{u}P_{eq} \rangle \langle c \rangle . \quad (10b)$$

The diffusive flux—the second term on the right-hand side of (10a)—is zero as one would expect for the local equilibrium distribution. Equation (10b) indicates that the solute velocity is

$$\mathbf{V} = \langle \mathbf{u}P_{eq} \rangle = [1/(1-\phi+\phi m^{-1})]\mathbf{U} . \quad (11)$$

The solute average velocity $\mathbf{V}$ differs from the bed average velocity $\mathbf{U}$, because the solute may preferentially partition into one of the two phases. In general the partition coefficient m, and therefore the solute average velocity will vary among different solute species; it is this effect which makes chromatographic separations possible.

We next seek the $O(\epsilon)$ diffusive contribution to the mass flux, which is driven by the $O(\epsilon)$ terms in (4). For c_1, in the expansion of the detailed concentration field, we have

$$\frac{\partial c_1}{\partial t} + \nabla \cdot \left(\mathbf{u}c_1 - \frac{D}{M}\nabla(Mc_1) \right) = -\frac{\partial c_0}{\partial T} - \nabla_{\mathbf{x}} \cdot \left(\mathbf{u}c_0 - \frac{D}{M}\nabla(Mc_0) \right) + \nabla \cdot \left(\frac{D}{M}\nabla_{\mathbf{x}}(Mc_0) \right) , \quad (12a)$$

with

$$\langle c_1 \rangle = 0 . \quad (12b)$$

Substituting the solution [Eq. (8)] for c_0, using the condition that P_{eq} is independent of T, for a statistically homogen-

eous media, the fact that $\langle c \rangle$ is independent of the microscale variable $\mathbf{x}$, and the macroconservation equation (5), the problem for c_1 becomes

$$\frac{\partial c_1}{\partial t} + \nabla \cdot \left(\mathbf{u} c_1 - \frac{D}{M} \nabla (M c_1) \right) = - \nabla_{\mathbf{x}} \cdot (\mathbf{v}'_m P_{eq} \langle c \rangle) , \tag{13}$$

where $\mathbf{v}'_m = \mathbf{v}_m - \mathbf{V}$ and $\mathbf{v}_m = \mathbf{u} - (1/P_{eq}) \nabla (D P_{eq})$. Here $\mathbf{v}_m$ is the velocity of the solute, which includes, in addition to the fluid velocity, a "drift" velocity which is nonzero only at the interphase boundaries where the molecular diffusivity undergoes a step change.

Note that the definition of $\mathbf{v}_m$ in (13) involves the product of $\nabla (D P_{eq})$, which contains a delta function at the solid surfaces, and $1/P_{eq}$, which undergoes a step change at the surfaces. Such an expression is not uniquely defined in the context of generalized functions.[7,8] However, we shall adopt the convention that the concentration takes on its fluid phase value at the interface. This choice affects the magnitude of $\mathbf{v}_m$, but does not affect the results [Eq. (17)] below that we shall obtain for the macroscopic transport coefficients as these always involve the product $\mathbf{v}_m$ with a quantity (P_{eq} or P) whose magnitude depends on the convention. The product of two generalized functions would not arise and an expresssion for the diffusivity equivalent to (17) could be derived if we simply did not define $\mathbf{v}_m$ in (13). However, the interpretation of $\mathbf{v}_m$ as the solute velocity including the drift resulting from variations in the molecular diffusivity will provide physical insight into the final expression (17) for the effective diffusivity. In physical terms the magnitude of $\mathbf{v}_m$ depends on whether we consider the drift to occur arbitrarily close to the interface on the fluid side or on the solid side.

The solution for c_1 can be written as

$$c_1 = - \nabla_{\mathbf{x}} \cdot \left(\int d\mathbf{x}_1 \int_{-\infty}^{t} dt_1 \, P(\mathbf{x},t \,|\mathbf{x}_1,t_1) \times \mathbf{v}'_m (\mathbf{x}_1,t_1) P_{eq} (\mathbf{x}_1) \langle c \rangle \right) , \tag{14}$$

where the transition probability or Green's function $P(\mathbf{x},t \,|\mathbf{x}_1,t_1)$ satisfies

$$\frac{\partial P}{\partial t} + \nabla \cdot \left(\mathbf{u} P - \frac{D}{M} \nabla (M P) \right) = \delta (\mathbf{x} - \mathbf{x}_1) \delta (t - t_1) . \tag{15}$$

The transition probability is the probability density for finding a tracer or solute particle at position $\mathbf{x}$ at time t if it was at position $\mathbf{x}_1$ at time t_1. The introduction of the transition probability reduces the transport problem to one involving a single tracer particle and thus provides a convenient physical basis for subsequent discussion. However, in general the solution of (15) is nontrivial and so (14) must be viewed as a formal solution.

The $O(\epsilon)$ contribution to the mass flux is

$$\langle \mathbf{q}_1 \rangle = \langle \mathbf{u} c_1 \rangle - \langle (D/M) \nabla (M c_1) \rangle - \langle (D/M) \nabla_{\mathbf{x}} (M c_0) \rangle . \tag{16}$$

Substituting for c_0 from (8) the last term in (16) is the product of the average concentration gradient and the ensemble average of the molecular diffusivity weighted with the equilibrium distribution, i.e., $- \langle D P_{eq} \rangle \nabla \langle c \rangle$. The second term on the right-hand side of (16) may be written in the form

$$- \nabla \langle D c_1 \rangle + \langle M c_1 \nabla (D/M) \rangle ,$$

where the first term in zero, because it is the microscale gradient of an averaged quantity, which only varies on the macroscale. Thus, using (14) for c_1 we can write (16) in the form

$$\langle \mathbf{q}_1 \rangle = - \nabla_{\mathbf{x}} \cdot (\mathsf{D} \langle c \rangle) , \tag{17a}$$

where

$$\mathsf{D} = \mathsf{I} \langle D P_{eq} \rangle + \left\langle \mathbf{v}'_m (\mathbf{x}) \int d\mathbf{x}_1 \times \int_{-\infty}^{t} dt_1 \, P(\mathbf{x},t \,|\mathbf{x}_1,t_1) \mathbf{v}'_m (\mathbf{x}_1) P_{eq} (\mathbf{x}_1) \right\rangle , \tag{17b}$$

or equivalently

$$\mathsf{D} = \mathsf{I} \langle D P_{eq} \rangle + \left\langle \mathbf{v}'_m (\mathbf{x}) P_{eq} (\mathbf{x}) \int d\mathbf{x}_1 \times \int_{-\infty}^{t} dt_1 \, P(\mathbf{x},t \,|\mathbf{x}_1,t_1) \mathbf{v}'_m (\mathbf{x}_1) \right\rangle , \tag{17c}$$

where I is the isotropic tensor. In porous media the solute velocity $\mathbf{v}_m$ and the equilibrium distribution P_{eq} are time independent, so the time integral in (17b) is trivial and (17b) may be written as

$$\mathsf{D} = \mathsf{I} \langle D P_{eq} \rangle + \left\langle \mathbf{v}'_m (\mathbf{x}) \int d\mathbf{x}_1 \, \rho (\mathbf{x}|\mathbf{x}_1) \mathbf{v}'_m (\mathbf{x}_1) P_{eq} (\mathbf{x}_1) \right\rangle , \tag{17d}$$

where ρ satisfies the steady form of (15) with the rhs replaced by $\delta (\mathbf{x} - \mathbf{x}_1)$.

According to (17) the effective diffusivity is equal to the average molecular diffusivity weighted by the equilibrium solute distribution, plus a velocity correlation function involving the solute velocity disturbance $\mathbf{v}'_m$. This solute velocity disturbance contains a drift velocity, because of jump in the diffusivity at the fluid–solid boundary, as well as the fluid velocity. In the absence of convection the drift velocity gives rise to the pure-conduction contribution to the effective diffusivity first studied by Maxwell[9] (Koch[6], Sec. IV A).

The determination of the solute average velocity $\mathbf{V}$ was straightforward, because P_{eq} is a constant in each phase and the configurational averaging of $\mathbf{u} P_{eq}$ is trivial. The same is not true of the determination of D from (17). The direct evaluation of the configurational average in (17) requires solving anew for each realization of the microstructure the fluid velocity $\mathbf{u}$ from the Navier–Stokes equations and the transition probability P. As shown in Koch *et al.*[10] for periodic microstructures, the configurational average reduces to an average over a unit cell and this direct method is possible. For more general disordered microstructures, however, such a direct method is clearly impractical. Instead, one must average *first*, by deriving averaged equations for $\mathbf{u}$, P, etc., and then seek to break the nonlinear average by an appropriate *closure* scheme. This is the procedure carried out in our studies of dispersion in disordered media,[1] where the closure was made by diluteness.

B. Lagrangian appoach

In this section we shall consider the definition of the macroscopic transport properties of a porous medium in terms of moments of the probability distribution for the location of a tracer or solute particle; a Lagrangian view as opposed to the Eulerian view of the previous section. Here, we define the solute average velocity as the long-time rate of increase in the solute's mean position, i.e.,

$$\mathbf{V}_L \equiv \lim_{t\to\infty} \frac{d}{dt} \langle \mathbf{x} \rangle_{\mathrm{L}} \,. \tag{18}$$

The effective diffusivity is defined as the rate of increase of the mean-squared displacement—a measure of the spread about the mean position, i.e.,

$$\mathsf{D}_{\mathrm{L}} \equiv \lim_{t\to\infty} \frac{d}{dt} \langle (\mathbf{x} - \langle \mathbf{x} \rangle)(\mathbf{x} - \langle \mathbf{x} \rangle) \rangle_{\mathrm{L}} \,. \tag{19}$$

Here, the position $\mathbf{x}$ of the tracer is a stochastic variable that is related to the tracer's velocity $\mathbf{v}(t)$ by

$$\mathbf{x} - \mathbf{x}_0 = \int_{t_0}^{t} dt_1 \, \mathbf{v}(t_1) \,. \tag{20a}$$

It can be shown (cf. van Kampen,[3] Sec. VIII 8) that the Langevin transport equation for the solute position embodied in (20a) is equivalent to the Fokker–Planck equation [Eq. (1)], if

$$\bar{\mathbf{v}} = \mathbf{v}_m = \mathbf{u} - (1/P_{\mathrm{eq}}) \nabla (D P_{\mathrm{eq}}) \tag{20b}$$

and

$$(\mathbf{v} - \bar{\mathbf{v}})^2 = D \delta (t - t_1) \mathsf{I} \,. \tag{20c}$$

The overbars indicate an average over the fluctuations in the stochastic tracer velocity $\mathbf{v}$ on the molecular scale; this is the molecular level ensemble average used in Langevin analyses to obtain the average behavior.

The angle brackets in the definitions [Eqs. (18) and (19)] indicate a tracer ensemble average. This tracer average involves both an average (indicated by $\langle\ \rangle$) over all possible configurations of the medium, and an average over all possible paths taken by a tracer in a single configurational realization of the medium, i.e., the "molecular" average defined in (20). The exact relationship between this tracer ensemble average and the "configurational" ensemble average $\langle\ \rangle$, which we defined in Sec. II A, depends on the amount of information on the history of the tracer's motion that we require to evaluate the argument of the average. If we need only know the tracer's present position, then the Lagrangian average of some property f of the tracer is

$$\langle f(t) \rangle_{\mathrm{L}} = \left\langle \int d\mathbf{x} \, \bar{f}(\mathbf{x},t) P(\mathbf{x},t \,|\mathbf{x}_0,t_0) \right\rangle . \tag{21}$$

If we require the tracer's position at two times t and t_1, then $\langle f(t,t_1) \rangle_{\mathrm{L}}$

$$= \left\langle \int d\mathbf{x} \int d\mathbf{x}_1 \, \bar{f}(\mathbf{x},t,\mathbf{x}_1,t_1) P(\mathbf{x},t;\mathbf{x}_1,t_1|\mathbf{x}_0,t_0) \right\rangle , \tag{22a}$$

$$= \left\langle \int d\mathbf{x} \int d\mathbf{x}_1 \, \bar{f}(\mathbf{x},t,\mathbf{x}_1,t_1) \times P(\mathbf{x}_1,t_1|\mathbf{x},t;\mathbf{x}_0,t_0) P(\mathbf{x},t \,|\mathbf{x}_0,t_0) \right\rangle . \tag{22b}$$

The latter average [Eq. (22)] is useful, for example, in obtaining the correlation between a property of the tracer at time t and another (or the same) property at time t_1. The transition probabilities appearing in (21) and (22) satisfy conservation relations analogous to (15).

To evaluate the Lagrangian tracer average velocity, we substitute (20) in (18) and take the time derivative

$$\mathbf{V}_{\mathrm{L}} = \lim_{t\to\infty} \langle \mathbf{v}(t) \rangle = \lim_{t\to\infty} \left\langle \int d\mathbf{x} \, \mathbf{v}_m(\mathbf{x},t) P(\mathbf{x},t \,|\mathbf{x}_0,t_0) \right\rangle . \tag{23}$$

Equation (15) for the transition probability is identical to the mass conservation equation (1) with an initial condition $P = \delta(\mathbf{x} - \mathbf{x}_0)$ at $t = t_0$. In the long-time limit, $t - t_0 \to \infty$, we can again use the method of multiple scales to solve for P. Thus, to first order in $\epsilon = l/L$

$$P(\mathbf{x},t \,|\mathbf{x}_0,t_0) = P_{\mathrm{eq}} \langle P(\mathbf{X},T \,|\mathbf{X}_0,T_0) \rangle \,, \tag{24}$$

where $\langle P \rangle$ has replaced $\langle c \rangle$ in (8a). Substituting in (23) in taking the average, we have

$$\mathbf{V}_{\mathrm{L}} = \int d\mathbf{x} \langle \mathbf{v}_m P_{\mathrm{eq}} \rangle \, \langle P(\mathbf{X},T \,|\mathbf{X}_0,T_0) \rangle = \langle \mathbf{v}_m P_{\mathrm{eq}} \rangle \,. \tag{25}$$

The final equality in (25) is obtained using the normalization of $\langle P \rangle$ to unity and the fact that $\langle \mathbf{v}_m P_{\mathrm{eq}} \rangle$ is constant in a homogeneous medium (the microscale spatial dependence of $\mathbf{v}_m P_{\mathrm{eq}}$ being smoothed in the averaging process). Comparing (25) with (11) and noting that

$$\langle (\mathbf{v}_m - \mathbf{u}) P_{\mathrm{eq}} \rangle = \nabla \langle D P_{\mathrm{eq}} \rangle = 0$$

shows the Lagrangian and Eulerian average velocities are identical in a homogeneous medium. In an inhomogenous medium $\langle \mathbf{v}_m P_{\mathrm{eq}} \rangle$, although smoothed on the microscale, is still a function of the macroscale variable $\mathbf{X}$, only the first equality in (25) holds, and the Lagrangian average velocity is obtained from a macroscale average of the Eulerian average velocity $\mathbf{V} = \langle \mathbf{v}_m P_{\mathrm{eq}} \rangle$, weighted with $\langle P(\mathbf{X},T \,|\mathbf{X}_0,T_0) \rangle$. The Lagrangian average velocity in an inhomogeneous medium is then the average Eulerian velocity experienced by a tacer at time T given that it was released at $\mathbf{X}_0$ at time T_0.

In order to evaluate the Lagrangian effective diffusivity, we first substitute (20a) for the position of the tracer and take the time derivative to give

$$\mathsf{D}_{\mathrm{L}} = \lim_{t\to\infty} \frac{1}{2} \left\langle \int_{t_0}^{t} dt_1 \, [\mathbf{v}'(t)\mathbf{v}'(t_1) + \mathbf{v}'(t_1)\mathbf{v}'(t)] \right\rangle_{\mathrm{L}} , \tag{26a}$$

$$= \lim_{t\to\infty} \mathrm{sym} \left\langle \mathbf{v}'(t) \int_{t_0}^{t} dt_1 \, \mathbf{v}'(t_1) \right\rangle_{\mathrm{L}} , \tag{26b}$$

where $\mathbf{v}'(t) = \mathbf{v}(t) - \mathbf{V}_{\mathrm{L}}$ and $\mathrm{sym}\, \mathsf{A} = \frac{1}{2}(\mathsf{A} + \mathsf{A}^{\dagger})$. Taking the molecular average using Eqs. (20b) and (20c)

$$\mathsf{D}_{\mathrm{L}} = \lim_{t\to\infty} \left(\langle D \mathsf{I} \rangle_{\mathrm{L}} + \mathrm{sym} \left\langle \mathbf{v}'_m(t) \int_{t_0}^{t} dt_1 \, \mathbf{v}'_m(t_1) \right\rangle_{\mathrm{L}} \right) . \tag{26c}$$

Using the second average [Eqs. (22a) and (22b)], the diffusivity can be written as

$$\mathsf{D}_L = \lim_{t\to\infty} \mathrm{sym}\Big(\Big\langle \int d\mathbf{x} \int d\mathbf{x}_1\, \mathbf{v}'_m(\mathbf{x},t) \int_{t_0}^{t} dt_1\, \mathbf{v}'_m(\mathbf{x}_1,t_1) \times P(\mathbf{x}_1,t_1|\mathbf{x},t;\mathbf{x}_0,t_0) P(\mathbf{x},t|\mathbf{x}_0,t_0) \Big\rangle + \Big\langle \int d\mathbf{x}\, D(\mathbf{x}) P(\mathbf{x},t|\mathbf{x}_0,t_0) \Big\rangle \Big) . \quad (27)$$

In the long-time limit $t - t_0 \to \infty$, we can substitute (24) for the transition probability $P(\mathbf{x},t|\mathbf{x}_0,t_0)$ in (27) and take the average to give

$$\mathsf{D}_L = \lim_{t\to\infty} \mathrm{sym} \int d\mathbf{x} \langle P(\mathbf{X},T|\mathbf{X}_0,T_0)\rangle \times \Big(\langle \mathsf{I} D(\mathbf{x}) P_{eq}(\mathbf{x})\rangle + \int d\mathbf{x}_1 \int_{t_0}^{t} dt_1 \times \langle \mathbf{v}'_m(\mathbf{x}) P_{eq}(\mathbf{x}) \mathbf{v}'_m(\mathbf{x}_1) P(\mathbf{x}_1,t_1|\mathbf{x},t;\mathbf{x}_0,t_0)\rangle \Big) , \quad (28)$$

where we have commuted the average with the integrations in $\mathbf{x}_1$ and t_1. We assume that a solute particle's position relative to the microstructure becomes uncorrelated in a time l/U, so that the second average in (28) is independent of the initial conditions $(\mathbf{x}_0,t_0)$ at long times $t - t_0 \gg l/U$, and the time integral converges for $t - t_1 \gg l/U$ to a result independent of t_0, to give

$$\mathsf{D} = \mathrm{sym} \int d\mathbf{x} \langle P(\mathbf{X},T|\mathbf{X}_0,T_0)\rangle \times \Big(\langle \mathsf{I} D(\mathbf{x}) P_{eq}(\mathbf{x})\rangle + \int d\mathbf{x}_1 \int_{-\infty}^{t} dt_1 \times \langle \mathbf{v}'_m(\mathbf{x}) P_{eq}(\mathbf{x}) \mathbf{v}'_m(\mathbf{x}_1) P(\mathbf{x}_1,t_1|\mathbf{x},t)\rangle \Big) . \quad (29)$$

As in (25) the variables within the second average are functions only of the microscale position in a homogeneous medium, and this microscale spatial dependence is smoothed by the average. Performing the X integration in (29) using the normalization condition on $\langle P\rangle$, then, gives

$$\mathsf{D}_L = \langle D P_{eq}\rangle \mathsf{I} + \mathrm{sym}\Big\langle \mathbf{v}'_m(\mathbf{x}) P_{eq}(\mathbf{x}) \int d\mathbf{x}_1 \times \int_{-\infty}^{t} dt_1\, \mathbf{v}'_m(\mathbf{x}_1) P(\mathbf{x}_1,t_1|\mathbf{x},t)\Big\rangle . \quad (30)$$

The Lagrangian diffusivity is seen to be equivalent to the symmetric part of the Eulerian diffusivity, $\mathsf{D}_L = \mathrm{sym}\,\mathsf{D}$.

In the preceding Lagrangian analysis we have assumed that a solute particle's position relative to the microstructure and, therefore, its velocity disturbance become uncorrelated with its initial position after a sufficiently long time. The same assumption is implicit in the multiple-scale analysis used to derive the Eulerian transport properties in Sec. II A, where it is required in order that the microtransport problem is truly occurring only on the small length and time scales. If this assumption does not hold, the result is a nondiffusive macroscopic transport process, which cannot be described by a constant solute velocity and effective diffusivity. Such processes are beyond the scope of the present analysis, requiring a nonlocal description.[5,6]

We have made the above derivations without any reference to the type of microstructure, simply relying on the multiple-scale analysis. Indeed, little reference was made to porous media and the results have a much wider applicability. The connection with the work of Brenner[11] for spatially periodic microstructures can also be made. In place of the micro- and macroscale variables $\mathbf{x}$ and $\mathbf{X}$, Brenner uses the designation local and global and *requires* that the local variable be bounded. With the multiple-scale analysis, no such boundedness is required and this restriction can be relaxed. Although derived from a different approach and written in different form, Brenner obtained essentially the same expressions for the solute velocity (25) and diffusivity (30) for the special case of a spatially periodic porous medium, when allowance is made for the configurational average reducing to an average over a unit cell. The basic microscale equations for P_{eq} [Eq. (8)] and c_1 or P [Eqs. (13) or (15)] are also analogous. Thus, we have a general framework in which to view transport processes in porous media, regardless of the details of the microstructure.

III. THE ANTISYMMETRIC EFFECTIVE DIFFUSIVITY RESULTING FROM FLOW THROUGH ANISOTROPIC MEDIA THAT LACK A CENTER OF REFLECTIONAL SYMMETRY

In Sec. II we noted that the Lagrangian and Eulerian definitions of the effective diffusivity are not equivalent, as is commonly assumed. Rather, the Eulerian diffusivity tensor contains an antisymmetric part, which is absent in the Lagrangian diffusivity. In this section we shall examine the physical significance of this antisymmetric diffusivity and the circumstances that give rise to it.

The antisymmetric part D^a of the effective diffusivity may be written as

$$\mathsf{D}^a = \boldsymbol{\epsilon}\cdot\mathbf{A} , \quad (31a)$$

where $\boldsymbol{\epsilon}$ is the permutation tensor. Using the definition $\mathsf{D}^a = \frac{1}{2}(\mathsf{D} - \mathsf{D}^\dagger)$ and (17b), the pseudovector $\mathbf{A}$ is

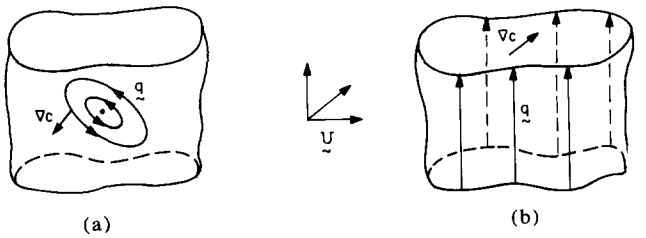
$$\mathbf{A} = \tfrac{1}{2}\Big\langle \int d\mathbf{x}_1 \int_{-\infty}^{t} dt_1 \mathbf{v}'_m(\mathbf{x}) \times \mathbf{v}'_m(\mathbf{x}_1) P_{eq}(\mathbf{x}_1) P(\mathbf{x},t|\mathbf{x}_1,t_1)\Big\rangle . \quad (31b)$$

The mass flux resulting from this antisymmetric diffusivity, then, may be written

$$\langle \mathbf{q}\rangle = -\mathsf{D}^a\cdot\nabla\langle c\rangle = -(\boldsymbol{\epsilon}\cdot\mathbf{A})\cdot\nabla\langle c\rangle = -\mathbf{A}\times\nabla\langle c\rangle , \quad (32)$$

indicating that the flux is perpendicular to the concentration gradient. Here, $\mathbf{A}$ appears as a pseudovector in Eq. (32) for the average mass flux, its sign depending on the relative handedness of the macroscale coordinates and the medium's structure. It will emerge that $\mathbf{A} = 0$ and $\mathsf{D}^a = 0$ when the medium possesses full reflectional symmetry so that the bed structure has no chirality.

As illustrated in Fig. 1, the flux runs parallel to the isoconcentration surfaces. If the isoconcentration surfaces are closed within the medium [as in Fig. 1(a)], then the antisymmetric diffusivity induces a circulation around the isoconcentration surfaces, but does not transport solute across the isoconcentration surfaces and so does not affect the concentration field. Furthermore, as this circulation of mass does not affect the concentration in an unbounded medium it cannot affect the mean-squared displacement of a tracer in an unbounded medium, explaining the absence of an anti-



(a) (b)

FIG. 1. The flux **q** resulting from antisymmetric diffusion is illustrated. The flux is perpendicular to ∇c and parallel to the isoconcentration surfaces. If the isoconcentration surfaces are enclosed in an unbounded medium (a), the antisymmetric diffusion does not affect the concentration. However, if the isoconcentration surface intersects the boundary of a finite medium (b), the antisymmetric diffusivity gives rise to an observable flux perpendicular to ∇c.

symmetric component in the Lagrangian effective diffusivity.

The flux resulting from the antisymmetric diffusivity *is* important in finite medium such as that shown in Fig. 1(b). If we impose concentration boundary conditions on the boundaries of the medium in such a way that there is a linear concentration gradient in the y direction, we shall observe a mass flux in the x direction—perpendicular to the imposed concentration gradient—between the two horizontal surfaces.

This phenomenon violates our intuitive expectation that a flux should not be perpendicular to its driving force. The Onsager reciprocal relations, which are based on thermodynamic fluctuation theory, microscopic reversibility, and an assumed linear reponse to driving forces (deGroot and Mazur[12]) require the diffusivity to be symmetric in a system near equilibrium in the absence of an external field.

Because of the convective motion in the present problem the system is not near equilibrium and the Onsager relations in their original form do not hold. However, we can develop similar relations concerning the symmetry properties of the diffusivity tensor. A crucial step in the derivation of the Onsager relations is invoking microscopic reversibility. In our dispersion problem, the appropriate "microscopic" point of departure is the transition probability $P(\mathbf{x},t\,|\mathbf{x}_1,t_1)$ in (15). The equation for the transition probability is reversible and a tracer particle retraces its trajectory upon time inversion only if we also reverse the convective field (van Kampen,[3] Sec. X.4), i.e.,

$$P(\mathbf{x},t\,|\mathbf{x}_1,t_1,U) = P(\mathbf{x}_1,t\,|\mathbf{x},t_1,-U)\ . \tag{33}$$

We also note that the solute velocity disturbance $\mathbf{v}'_m$ contains a convective part $\mathbf{u}'$ which reverses sign upon reversal of U, and a conductive part $\mathbf{w} = -(1/P_{eq})\nabla(DP_{eq})$ which is invariant under reversal of U.

The effective diffusivity (17) can be written in the form

$$\mathsf{D} = \mathsf{D}_m + \mathsf{D}_{ww} + \mathsf{D}_{uu} + \mathsf{D}_{wu}\ , \tag{34a}$$

where

$$\mathsf{D}_m = \langle DP_{eq}\rangle \mathsf{I} \tag{34b}$$

is the average molecular diffusivity,

$$\mathsf{D}_{ww} = \left\langle \mathbf{w}(\mathbf{x}) \int d\mathbf{x}_1 \int_{-\infty}^{t} dt_1\, P(\mathbf{x},t\,|\mathbf{x}_1t_1)P_{eq}(\mathbf{x}_1)\mathbf{w}(\mathbf{x}_1)\right\rangle \tag{34c}$$

is the contribution from the drift velocity as a result of the jump in the molecular diffusivity of the solute at the interphase boundaries,

$$\mathsf{D}_{uu} = \left\langle \mathbf{u}'(\mathbf{x}) \int d\mathbf{x}_1 \int_{-\infty}^{t} dt_1\, P(\mathbf{x},t\,|\mathbf{x}_1t_1)P_{eq}(\mathbf{x}_1)\mathbf{u}'(\mathbf{x}_1)\right\rangle \tag{34d}$$

is the convective contribution, and

$$\mathsf{D}_{uw} = \mathrm{sym}\left\langle \mathbf{u}'(\mathbf{x}) \int d\mathbf{x}_1 \int_{-\infty}^{t} dt_1\, P(\mathbf{x},t\,|\mathbf{x}_1t_1)P_{eq}(\mathbf{x}_1)\mathbf{w}(\mathbf{x}_1)\right\rangle \tag{34e}$$

is a cross term involving correlations between the drift velocity as a result of molecular diffusivity variations and the fluid velocity.

Using the properties of the transition probability and solute velocity under reversal of the bulk velocity, we find that

$$\mathsf{D}_{uu}(U) = \mathsf{D}^{\dagger}_{uu}(-U)\ , \tag{35a}$$

$$\mathsf{D}_{ww}(U) = \mathsf{D}^{\dagger}_{ww}(-U)\ , \tag{35b}$$

$$\mathsf{D}_{wu}(U) = -\mathsf{D}_{wu}(-U) = \mathsf{D}^{\dagger}_{wu}(U)\ , \tag{35c}$$

and

$$\mathsf{D}_m(U) = \mathsf{D}_m(-U) = \mathsf{D}^{\dagger}_m(U)\ . \tag{35d}$$

Equations (35a) and (35b) allow the possibility of an antisymmetric component of the diffusivity in the presence of convection in porous media. [Note that the bulk convection may affect the conductive contribution D_{ww} through its influence on the transition probability, so that in (35b) $\mathsf{D}_{ww}(U) \neq \mathsf{D}_{ww}(-U)$.]

The phenomenon of a mass flux perpendicular to the concentration gradient in flow through porous media is analogous to the Hall effect, in which an electric flux perpendicular to the imposed electric field is induced by an external magnetic field. In the former case the average velocity causes the Onsager relations to take on the modified form (35); in the latter case the magnetic field plays this role.

While the modified Onsager relations (35) do not require the diffusivity to be symmetric, they do restrict the class of media that can exhibit a nonsymmetric diffusivity. Equation (35a) requires the antisymmetric part of the diffusivity to be an odd function of the average velocity. If the medium has reflectional symmetry about a plane perpendicular to the direction of the average flow, then the diffusivity cannot depend on the sign of the average velocity, i.e., it must be an even function of the average velocity. Thus, the antisymmetric diffusion component is present only in media that lack a center of reflectional symmetry. A center of reflectional symmetry is a point formed by the intersection of three orthogonal planes of reflectional symmetry. The absence of a center of symmetry is also the criterion for the fluid to exert a net torque on the solid structure of a porous medium (Brenner[13]). A disordered medium may possess reflectional symmetry even if its component grains do not, provided the grains' orientation distribution is symmetric.

IV. EXAMPLE: A SIMPLE CUBIC ARRAY OF SCREW PROPELLERS

In order to illustrate the antisymmetric diffusivity component found in beds that lack reflectional symmetry, we shall consider a bed of screw propellers with their axes oriented in the same direction. The screw propeller is illustrated in Fig. 2 and was described in Brenner.[13] The propeller consists of two thin disks of radii b whose centers are a distance s from the center of the unit cell. The two disks are joined by a thin rod perpendicular to their normals. They are rotated about this rod by an angle 2θ relative to each other. Flow past such an object exerts both a force and a torque (Brenner[13]):

$$\mathbf{f} = -\mu \mathsf{K}\cdot\mathbf{U}, \quad \mathbf{t} = -\mu \mathsf{C}\cdot\mathbf{U}, \tag{36}$$

where $\mathbf{f}$ is the force, $\mathbf{t}$ the torque,

$$\mathsf{K} = \tfrac{32}{3} b\,[\mathbf{1}_x\mathbf{1}_x(2+\cos^2\theta) + \mathbf{1}_y\mathbf{1}_y(2+\sin^2\theta) + 2\mathbf{1}_z\mathbf{1}_z],$$

$$\mathsf{C} = -\tfrac{32}{3} bs(\mathbf{1}_x\mathbf{1}_x - \mathbf{1}_y\mathbf{1}_y)\sin\theta\cos\theta,$$

and $\mathbf{1}_x$ is the unit vector in the x direction. In a porous medium of such objects, K is related to the permeability tensor and C to the "chirality" or handedness tensor, reflecting that a macroscopic torque must be exerted on the medium to keep it from rotating. We shall assume that the size s of the propellers is small compared to the lattice spacing h so that we may neglect interparticle hydrodynamic interactions.

The configurational ensemble average (2) takes on a simple form in ordered media. The only information required to specify the configuration of a periodic medium is the position of the point of interest $\mathbf{x}$ within the unit cell. Thus, the ensemble average is simply a volume average over the unit cell and the Eulerian effective diffusivity [Eq. (17d)] is given by

$$\mathsf{D} = \frac{1}{h^3}\int_{\text{unit cell}} d\mathbf{x}\Big(\mathsf{I}\,DP_{\text{eq}} + \mathbf{v}'_m(\mathbf{x})\int d\mathbf{x}_1\,\rho(\mathbf{x}|\mathbf{x}_1)\mathbf{v}'_m(\mathbf{x}_1)P_{\text{eq}}(\mathbf{x}_1)\Big). \tag{37}$$

Neglecting the effects of variations in the molecular diffusivity and solubility of the tracer, $D = D_f$, $P_{\text{eq}} = 1$, (37) reduces to

$$\mathsf{D} = \mathsf{I} + \text{Pe}^2\int_{\text{unit cell}} d\mathbf{x}\,\mathbf{u}'(\mathbf{x})\int d\mathbf{x}_1\,\rho(\mathbf{x}|\mathbf{x}_1)\mathbf{u}'(\mathbf{x}_1), \tag{38}$$

where here and in subsequent expressions all lengths have been nondimensionalized by the lattice spacing h, the effective diffusivity with the molecular diffusivity D_f, and the drag and torque by μh and μh^2, respectively.

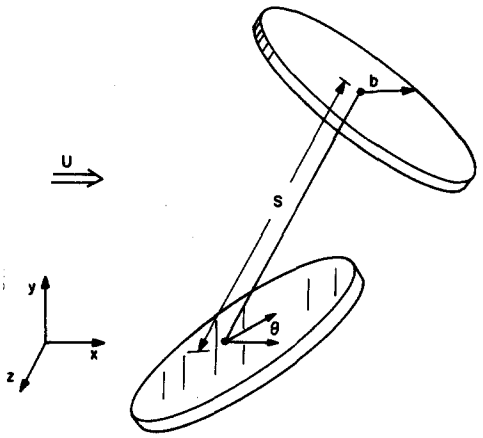


FIG. 2. A prospective view of a screw propeller, which consists of two circular disks connected by a thin rod parallel to the z direction. The disk in the foreground is rotated from the xz plane through an angle θ, while the one in the background is rotated through an angle $-\theta$. The average flow $\mathbf{U}$ is in the x direction.

It is convenient to introduce the finite Fourier transform

$$\hat{\mathbf{u}}'(\mathbf{k}) = \int_{\text{unit cell}} d\mathbf{x}\, e^{-2\pi i\mathbf{k}\cdot\mathbf{x}}\mathbf{u}'(\mathbf{x}),$$

and its inverse

$$\mathbf{u}'(\mathbf{x}) = \sum_{\mathbf{k}} e^{2\pi i\mathbf{k}\cdot\mathbf{x}}\,\hat{\mathbf{u}}'(\mathbf{k}),$$

where the sum is over all $\mathbf{k} = (1/h)(b_1\mathbf{n}_1 + b_2\mathbf{n}_2 + b_3\mathbf{n}_3)$, b_1, b_2, and b_3 are integers, and $\mathbf{n}_1$, $\mathbf{n}_2$, and $\mathbf{n}_3$ are axes of the reciprocal lattice, which in the present case of a cubic array coincide with the axis of the real lattice.

Using the convolution theorem the effective diffusivity (38) may be written as

$$\mathsf{D} = \mathsf{I} + \text{Pe}^2\sum_{\mathbf{k}}\hat{\mathbf{u}}'(-\mathbf{k})\hat{\rho}(\mathbf{k})\hat{\mathbf{u}}'(\mathbf{k}). \tag{39}$$

Far enough away from the center of the unit cell the velocity disturbance may be approximated as that caused by a point force and a point torque,

$$\hat{\mathbf{u}}' = (\mathbf{f} + 2\pi i\mathbf{t}\times\mathbf{k})\cdot[\mathsf{I} - (\mathbf{kk}/k^2)]/4\pi^2k^2. \tag{40}$$

Far from the center of the unit cell where the velocity disturbance is small compared to the average velocity $\mathbf{U}$, the transition probability ρ satisfies [cf. Eq. (15)]

$$\nabla\cdot(\text{Pe}\,\mathbf{U}\rho - \nabla\rho) = \delta(\mathbf{x}-\mathbf{x}_1). \tag{41}$$

Taking the Fourier transform we obtain

$$\hat{\rho} = 1/(i\,\text{Pe}\,\mathbf{U}\cdot\mathbf{k} + k^2). \tag{42}$$

The effective diffusivity, obtained by inserting (40) and (42) for the velocity disturbance and transition probability in (39), rationalizing the denominator, and dropping the imaginary terms, which sum to zero, is

$$\mathsf{D} = \mathsf{I} + \frac{\text{Pe}^2}{16\pi^4}\sum_{\mathbf{k}\neq 0}\left(\frac{\mathbf{f}\cdot[\mathsf{I}-(\mathbf{kk}/k^2)]^2 + 4\pi^2(\mathbf{t}\times\mathbf{k})^2}{k^2[4\pi^2k^4 + \text{Pe}^2(\mathbf{k}\cdot\mathbf{U})^2]}\right) + \frac{\text{Pe}^3}{16\pi^4}\sum_{\mathbf{k}\neq 0}\left(\frac{\{\mathbf{f}\cdot[\mathsf{I}-(\mathbf{kk}/k^2)]\cdot(\mathbf{t}\times\mathbf{k}) - (\mathbf{t}\times\mathbf{k})\cdot\mathbf{f}\cdot[\mathsf{I}-(\mathbf{kk}/k^2)]\}\mathbf{k}\cdot\mathbf{U}}{k^4[4\pi^2k^4 + \text{Pe}^2(\mathbf{k}\cdot\mathbf{U})^2]}\right). \tag{43}$$

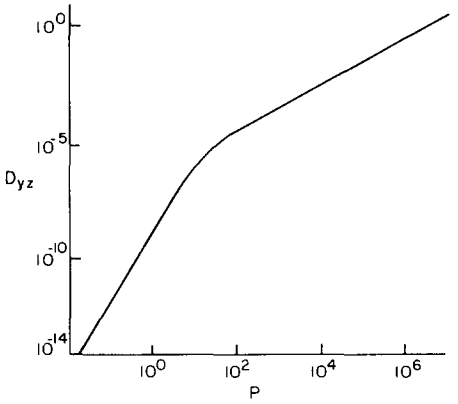


FIG. 3. The antisymmetric diffusivity $D^a_{yz} = -D^a_{zy}$, where $\mathsf{D}^a = \frac{1}{2}(\mathsf{D} - \mathsf{D}^\dagger)$, caused by flow parallel to the x axis in a cubic array of screw propellers (illustrated in Fig. 2) is plotted as a function of the Peclet number for $s/h = 0.1$ and $b/h = 0.01$.

The first term in (43) is the conventional symmetric contribution to the effective diffusivity similar to that calculated by Koch *et al.*[10] The second term, however, is antisymmetric. This antisymmetric diffusivity gives a component of the mass flux perpendicular to the imposed concentration gradient. To see how this occurs let us consider a single screw propeller. If the flow is in the x direction and the concentration gradient is in the z direction as indicated in Fig. 2, there is a component of the mass flux in the y direction. This flux occurs because the disk in the foreground directs fluid of relatively high concentration upward, while the disk in the background directs fluid of lower concentration downward, resulting in a net upward (positive y direction) flux of solute with no net flux of fluid. When all the screw propellers in a bed are oriented in one direction the combined effect is to give a macroscopic mass flux perpendicular to the macroscopic concentration gradient. Note, the spatial distribution of the screw propellers can be random, i.e., a disordered medium, and there will still be an antisymmetric diffusivity if the orientation of the propellers is not random. That is, for any porous medium in which a macroscopic torque must be exerted there will be an antisymmetric diffusivity.

The component $D^a_{yz} = -D^a_{zy}$ of the antisymmetric diffusivity, the second term in (43), which is responsible for the phenomenon described above, is plotted as a function of the Peclet number in Fig. 3. At high Peclet numbers this antisymmetric diffusivity is purely mechanical and grows as Pe. At low Peclet numbers the leading order diffusive behavior, which is $O(\mathrm{Pe}^2)$, results from the velocity correlation function when a tracer samples the microstructure primarily by molecular diffusion. As this diffusive sampling has no directionality imposed by the bulk convection, the leading order diffusivity is purely symmetric. The antisymmetric diffusivity is $O(\mathrm{Pe}^3)$ at low Peclet numbers, resulting from the convective correction to the purely diffusive samping that results from including the convective term in Eq. (41) for the transition probability. The other components $D^a_{xy} = -D^a_{yx}$ and $D^a_{xz} = -D^a_{xz}$ of the antisymmetric diffusivity being odd in the x component of $\mathbf{k}$ sum to zero.

[1] D. L. Koch and J. F. Brady, J. Fluid Mech. **154**, 399 (1985).
[2] D. L. Koch and J. F. Brady, AIChE J. **32**, 158 (1986).
[3] N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1983).
[4] J. B. Keller, in *Statistical Mechanics and Statistical Methods in Theory and Applications*, edited by U. Landman (Plenum, New York, 1977), p. 631.
[5] D. L. Koch and J. F. Brady, J. Fluid Mech. (in press).
[6] D. L. Koch, Ph.D. thesis, Massachusetts Institute of Technology, 1986.
[7] M. J. Lighthill, *Fourier Analysis and Generalized Functions* (Cambridge U. P., Cambridge, 1980).
[8] D. S. Jones, *Generalized Functions* (McGraw-Hill, New York, 1966).
[9] J. C. Maxwell, *Electricity and Magnetism* (Clarendon, New York, 1873).
[10] D. L. Koch, R. G. Cox, H. Brenner, and J. F. Brady, to be submitted.
[11] H. Brenner, Chem. Eng. Sci. **19**, 599 (1964).
[12] S. R. deGroot and P. Mazur, *Nonequilibrium Thermodynamics* (Dover, New York, 1984), p. 35.
[13] H. Brenner, Philos. Trans. R. Soc. London Ser. A **297**, 81 (1980).